

COATINGS AND ENAMELS

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EFFECT OF ZINC AND TIN OXIDES ON THE BACTERICIDAL PROPERTIES OF GLASS ENAMEL COATINGS

O. V. Savvova¹Translated from *Steklo i Keramika*, No. 7, pp. 37–40, July, 2014.

The possibility of using zinc and tin oxides as antimicrobial agents in bactericidal glass enamel coatings is examined. The dependence of the inhibitory power of glass enamel coatings based on zinc and tin oxides on the CFU concentration of *E. Coli* is determined. The optimal amount of zinc and tin oxides imparting a strong antibacterial effect to glass enamel coatings under the conditions of a severe bacterial infection is determined.

Key words: bactericidal properties, glass enamel coatings, zinc and tin oxides.

An important social problem is protecting the public from harmful and occasionally fatal pathogenic microorganisms. Neutralization of antibiotic-resistant bacteria is a problem in many countries. For example, according to UN data for 2009 every European visiting a hospital can acquire bacterial and viral infections. This makes it necessary to provide antibacterial protection in public locations: hospitals (operating and resuscitation wards, maternity and infectious diseases wards, medical and pharmaceutical laboratories), public dining areas (food preparation units, refrigeration equipment, tanks for storing and heating water, plumbing fixtures), the metro and elsewhere [1]. In connection with the need for protection from the harmful effects of bacteria and fungi and their metabolites more attention is being focused on the development and use of materials with antibacterial properties in different industries and in daily life: plastics and special glass as well as composite, metallic, polymer, glass ceramic and glass enamel coatings [2].

The efficacy and prospects for using glass enamel coatings in particular are due to their considerable advantages over other materials [3, 4]. The antibacterial effect of enamel coatings is largely due to added silver ions. Silver ions are characterized by high affinity to sulfur and block the active catalytic centers of enzymes [5]. However, as a bactericide, silver not only increases the cost of enameled products considerably but it also can accumulate in people's bodies. This

results in the appearance of argyria and a number of chronic illnesses. For this reason the use of silver as a bactericide is not always warranted [6].

The creation of bactericidal glass enamel coatings for reliable long-term protection of steel parts and assorted articles require fundamentally new approaches to the development coatings. Validation of the choice of toxicants of pathogenic microorganisms and the mechanism of their inhibitory effect will make it possible to obtain glass enamel coatings with high sanitary-hygienic specifications and a significant bactericidal effect. All this requires fundamental research directed at the development of new-generation long-life antibacterial coatings based on glass enamels.

An effective method of increasing the competitiveness of glass enamels is to develop coatings affording prolonged action with respect to a wide spectrum of bacteria by using inexpensive and environmentally safe biocides in the enamels, specifically, zinc and tin oxides.

The great promise in using zinc oxide, which is used in different spheres of industry, medicine and pharmacology and agriculture, for synthesizing bactericidal glass enamel coatings is explained by the unique combination of its physical, chemical and biological properties. It is well known that zinc oxide is characterized by selective toxicity with respect to pathogenic bacteria, for example, intestinal bacteria [6], suppresses the growth of fungi and has a minimal toxic effect on human cells [7]. In the silicate industry zinc oxide can be used in the production of wear resistant and self-cleaning ceramics (dinnerware, pipes, bathroom-and-lavatory equip-

¹ National Technical University – Kharkov Polytechnic Institute, Kharkov, Ukraine (e-mail: savvova_oksana@ukr.net).

ment, stoves and so on) [8] and antibacterial glass ceramic coatings [9].

The advances made in the use of zinc oxide as a bactericidal agent in glass enamels pertain mainly to media with a high concentration of pathogenic microorganisms, specifically, *Escherichia Coli* (in what follows, *E. Coli*). At the same time the actual utilization conditions of enameled household articles are characterized by an external medium with CFU (colony forming units) *E. Coli* = 10^3 cells/ml [10].

For this reason our aim in the present work was to determine the efficacy of zinc oxide for media with CFU = 10^3 cells/ml as well as the possibility of using tin oxide as bactericidal fillers in glass enamel coatings.

EXPERIMENTAL PROCEDURE

The bactericidal and fungicidal properties of glass coatings were determined by means of bacteriological investigations of opportunistic pathogens using solid and liquid media by diffusion [11, 12] and quantitative [13] methods.

The fractional composition of the synthesized powders was determined by granulometric analysis in a Mastersizer 2000 particle size analyzer.

PRINCIPLES OF SYNTHESIS OF BIOCIDAL GLASS COATINGS

The production of antibacterial glass enamel coatings is based on the idea of combining polyfunctional glass enamel coatings with the bactericidal action of heavy-metal cations [14].

To obtain antibacterial glass coatings as oligodynamic components we picked the cations Zn^{2+} and Sn^{4+} , which manifest toxic action with respect to pathogenic microorganisms in concentrations not exceeding the permissible levels of migration (PLM) for humans [15] and for comparison the cation Ag^+ as a well-known bactericidal agent.

The antibacterial activity of zinc and tin oxides is realized by the suppression of microorganisms by the following mechanisms:

- oxidation and decomposition of organic components of bacteria by a photocatalytic pathway under the action of UV radiation [16];
- oxidation of structural enzymes and proteins as a result of the release of free ions adsorbed on cell surfaces [17];
- oxidation of structural enzymes and proteins by a catalytic pathway as a result of the release of H_2O_2 [16 – 18].

PRODUCTION OF GLASS COATINGS

Zinc and tin oxides, synthesized by chemical precipitation, with particle size of the order of 100 nm were picked as bactericidal fillers. An $AgNO_3$ solution was used to introduce Ag^+ .

The bactericidal cations were introduced in the form of presynthesized ZnO and SnO_2 nanopowders in the amounts (mass fraction) 1, 4 and 6% per 100% frit into glass enamel during milling of the frit. $AgNO_3$ was introduced in the amount 0.1% per 100% slip.

To determine the efficacy of introducing zinc and tin oxides as bactericidal components into enamels a titanium-containing covering frit was chosen for the glass matrix. The enamel slip based on the titanium-containing covering fit and bactericidal fillers were deposited on a primed metal and fired at temperature 840°C. The density of the slip was 1.68 g/cm^3 and the coverage was 8.0 g/dm^2 .

The glass enamel coatings obtained with the maximum ZnO content 1, 4 and 6% were labeled as BPZ 1, BPZ 4 and BPZ 6, with SnO_2 content 1, 4 and 6% as BPS 1, BPS 4 and BPS 6 and with 0.1% $AgNO_3$ as BPAg, respectively.

INVESTIGATION OF BACTERICIDAL PROPERTIES OF GLASS ENAMEL COATINGS

The study of the suppression properties of the experimental glass enamel coatings containing ZnO , SnO_2 and $AgNO_3$ showed that their suppression effects with respect to *E. Coli* on solid and liquid media are different.

Using the diffusion method on a scale for determining the bactericidal action of materials, i.e., the size of the growth suppression zone with measurement of the diameter of the suppression zone around a disk and the index of efficacy of the antibacterial properties [12], it was determined that an BPAg glass enamel coating did not show bactericidal action with respect to these bacteria. When 1% (mass fraction) zinc and tin oxides were introduced significant bactericidal action of the glass enamel coatings BPZ and BPS 1 was observed with diameter of the grown suppression zone for *E. Coli* equal to about 20 mm.

To determine the suppression capacity of glass enamel coatings, containing tin and zinc oxides with content 1 wt.% per 100% frit, the quantitative method was used under conditions of bacterial contamination to choose the initial CFU *E. Coli* concentration $10^3 - 10^7$ cells/ml; the exposure time was 24 h.

The need to investigate the bactericidal activity of glass enamel coatings with CFU < 10^7 cells/ml is explained by modeling conditions close to the operating conditions of glass enamel coatings which are characterized by negligible growth of the CFU *E. Coli* = $10^3 - 10^4$ cells/ml.

It was determined on the basis of an evaluation of the suppression capacity of BPZ 1 and BPS 1 coatings with different CFU *E. Coli* that the bactericidal action of active zinc and tin cations increases with increasing initial CFU *E. Coli* concentration at the start of exposure (Table 1). It was determined that the strongest bactericidal effect is manifested by the coating BPS 1 relative to the growth of a pure *E. Coli* culture (K_{culture}) with initial concentration CFU = 1.1×10^7 cells/ml.

TABLE 1. Suppression Action of Glass Enamel Coatings BPZ 1 and BPS 1 with Initial Concentration CFU E. Coli $10^3 - 10^7$ cells/ml

Glassy coatings and $K_{culture}$	Exposure	Concentration CFU E. Coli, cells/ml				
	Exposure start	1.1×10^7	3.2×10^6	1.2×10^5	5.0×10^4	2.2×10^3
$K_{culture}$	After exposure for 24 h	11.83×10^9	13.65×10^8	1.36×10^7	9.40×10^5	9.10×10^5
BPS 1		8.04×10^9	13.65×10^8	1.26×10^7	9.30×10^5	8.90×10^5
BPZ 1		9.10×10^9	11.83×10^8	1.23×10^7	8.90×10^5	8.25×10^5

This fact can be explained as follows. As the initial concentration CFU E. Coli increases, the efficacy of the bactericidal action of active cations increases because the contact area between the pathogenic microorganism and the glassy coating increases, and a possibility is created for increasing the activity of the bactericidal components as a result of a reduction of energy transfer between the microbes within the limits of the action of the suppression factors.

To determine the effect of the content of zinc and tin oxides on the suppression capacity (antibacterial effect) of E. Coli with CFU 1.1×10^7 cells/ml the bactericidal action of coatings with zinc and tin oxide contents 4 and 6 wt.% was evaluated by the quantitative method with exposure time 24 h.

**Suppression Action of Glass Enamel Coatings
for Initial Concentration CFU E. Coli = 10^7 cell/ml
after Exposure for 24 h**

BNZ 4	2.2×10^9
BPS 4	11.02×10^8
BPZ 6	2.2×10^9
BPS 6	11.17×10^8
$K_{culture}$	11.83×10^9

It was determined on the basis of these studies that the activity of E. Coli decreased relative to $K_{culture}$ by a factor of about 5 for the coating BPZ 4 and 10 for BPS 4. As ZnO and SnO₂ content in the coatings (BPZ 6 and BPS 6) continues to increase the value of CFU E. Coli under the experimental conditions remains practically unchanged. Therefore, introducing 4% (mass fraction) of zinc and tin oxides above 100% frit makes it possible to obtain glass enamel coatings characterized by a different antibacterial effect with the growth of the E. Coli colonies decreasing by 80 – 90% under the conditions of severe bacterial contamination with initial concentration CFU E. Coli = 10^7 cells/ml (see Fig. 1).

The results make it possible to choose the optimal concentration of bactericidal fillers to obtain antibacterial glass enamel coatings with respect to E. Coli with CFU $10^3 - 10^7$ cells/ml.

To eliminate the toxic effect of the glass enamel coatings BPZ 4 and BPS 4 the mass concentration (mg/liter) of Zn²⁺ and Sn⁴⁺ in the analyzed solutions was determined after boiling the coatings for 48 h in distilled water.

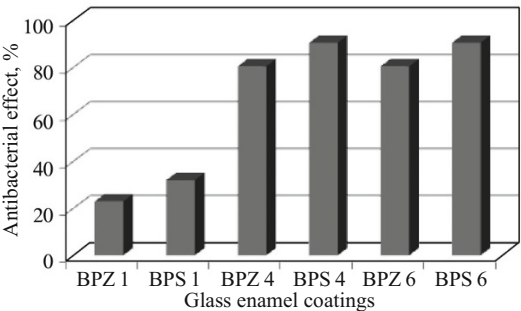


Fig. 1. Antibacterial effect of glass enamel coatings.

According to the results of the atomic-adsorption method the mass concentrations of Zn²⁺ and Sn⁴⁺ in solutions are 0.05 and 0.03 mg/liter and do not exceed the permissible migration levels for enamels intended for dinnerware [19]. The results of the investigations attest that zinc and tin oxides are nontoxic to humans and can be used as bactericidal fillers in glass enamel coatings.

CONCLUSIONS

The fundamental possibility of using zinc and tin oxides as biocidal agents to obtain bactericidal glass enamel coating with respect to E. Coli was validated. The dependence of the suppression capacity of glass enamel coatings based on zinc and tin oxides on their amount in the initial glass matrix and the CFU concentration of E. Coli was determined. The optimal amount of zinc oxide and tin oxide in glass enamel coatings making it possible to secure 80 and 90% antibacterial effects under conditions of severe bacterial contamination was determined. The principles established for synthesizing ecologically safe bactericidal glass enamel coatings can be used effectively to develop glassy materials that suppress the toxic effect of pathogenic microorganisms and to protect against biocorrosion of steel articles used for household and architectural purposes.

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